

**SYNTHESIS AND CHARACTERISATION OF NEW  
Ru<sub>3</sub> AND Os<sub>3</sub> CLUSTERS WITH SULPHUR  
CONTAINING PHOSPHINES, ALKYNE, AND  
ANTIMONY LIGANDS**

**HAFIZ MALIK HUSSIEN ABDELNASIR**

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CONTAINING PHOSPHINES, ALKYNE, AND  
ANTIMONY LIGANDS**

**by**

**HAFIZ MALIK HUSSIEN ABDELNASIR**

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## LIST OF ABBREVIATIONS

Å	angstrom
a, b, c	unit cell dimensions
anal	analysis atoms standard
ax	axial
ax	exial
BPK	sodium benzophenone ketyl radical anion $\text{Na}^+[\text{PhCOPh}]^{\cdot -}$
bpy	bipyridine
(bpcd)	4,5-bis(diphenyl-phosphino)-4-cyclopenten-1,3-dione
Bu <sup>t</sup>	tertbutyl -C(CH <sub>3</sub> ) <sub>3</sub>
Calc	calculated

°C	degree Centigrade
cm	centimetre ( $10^{-2}$ m)
cm <sup>3</sup>	cubic centimetre
Cp	cyclopentadienyl
dcpm	Bis(dicyclohexylphosphino)methane
dpae	1,2-bis(diphenylarsino)ethane
dpam	bis(diphenylarsino)methane
dppa	bis(diphenylphosphino)acetylene
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene $\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)_2$
dppm	bis(diphenylphosphino)methane
e	electron
eq	equatorial

et	ethyl
ffars	1,2-bis(dimethylarsino)butaflouro-cyclobutene
ffos	1,2-bis(diphenylphosphino)butaflouro-cyclobutene
f <sub>6</sub> fos	1,2-bis(diphenylphosphino)hexaflouro-cyclohexene
g	gram
h	hour
Hz	hertz
IR	infrared
J	coupling constant
L	general monodentate ligand
L-L	general bidentate ligand

m.p	melting point
mapm	diphenyl(o-N,N-dimethylanilyl) phosphine
Me	methyl
mg	milligram
MHz	megahertz
min	minutes
ml	milliliter
mmol	millimole
mol	mole
OD <sub>b</sub>	Optical density of the blank
OD <sub>n</sub>	Optical density of the negative control
OD <sub>s</sub>	Optical density of the samples

ORTEP	Oak Ridge Thermal Ellipsoid Plot
Ph	phenyl
ppm	part per million
PPN <sup>+</sup>	bis(triphenylphosphino) iminium (Ph <sub>3</sub> P) <sub>2</sub> N <sup>+</sup>
Pr <sup>i</sup>	iso-propyl
R	alkyl
R <sub>f</sub>	retention factor
SADABS	Siemens Area Detector Absorption Correction
SAINT	Siemens Analytical X-ray Area-detector Integration
sec	seconds
THF	tetrahydrofuran
TLC	thin layer chromatography

TMS	tetramethylsilane
$\alpha, \beta, \gamma$	unit cell angles
$\mu$	bridging bonding mode
NMR	nuclear magnetic resonance
$^{13}\text{C}$	carbon-13 isotope
d	doublet
dd	doublet of doublet
dt	doublet of the triplet
$^1\text{H}$	proton
m	multiplet
q	quartet
s	singlet



t	triplet
td	triplet of the doublet

**SINTESIS DAN PENCIRIAN GUGUSAN Ru<sub>3</sub> DAN Os<sub>3</sub> DENGAN  
SULFUR YANG MENGANDUNGI LIGAN PHOSPHINA, ACETILENA,  
DAN ANTIMONI**

**ABSTRAK**

Dua puluh empat kompleks gugusan baharu; dua puluh satu kompleks gugusan triruthenium carbonil, tiga kompleks gugusan triosmium carbonil dan empat ligan telah berjaya disintesis dan dicirikan menggunakan kaedah analisis unsur, dan kaedah spektroskopi, merangkumi IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR dan <sup>31</sup>P NMR spektroskopi. Struktur molekul produk telah ditentukan oleh kristal tunggal pembelauan sinar-X kecuali Ru<sub>3</sub>(CO)<sub>10</sub>(dpae). Dua ligan isomer daripada C<sub>19</sub>H<sub>17</sub>PS; iaitu PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SMe dan Ph<sub>2</sub>PCH<sub>2</sub>SPh. Dua ligan antimoni Sb(C<sub>6</sub>H<sub>4</sub>-3-OCH<sub>3</sub>)<sub>3</sub> dan Sb(C<sub>12</sub>H<sub>9</sub>)<sub>3</sub> digunakan bagi membentuk gugusan baharu. Satu sebatian antimony [Sb((C<sub>6</sub>H<sub>4</sub>)SCH<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] diuji bagi potensi anti-kanser terhadap beberapa jalur sel kanser manusia, iaitu kolon kanser (HCT- 116 and HT-29), kanser payudara (MCF-7), dan leukemia (K-562), sel kolon normal manusia (CCD-18Co) digunakan sebagai kawalan bagi model jalur sel normal. Keputusan menunjukkan sebatian yang diuji mempamerkan kesan anti-proliferatif terhadap semua jalur sel kanser. Keputusan ujian sitotoksiti boleh menjadi panduan kepada penemuan ubat. Tindak balas Ru<sub>3</sub>(CO)<sub>12</sub> dan Os<sub>3</sub>(CO)<sub>12</sub> dengan kedua-dua ligan sulfur fosforus menghasilkan tiga gugusan monotertukarganti;

$\text{Ru}_3(\text{CO})_{11}\text{PPh}_2\text{C}_6\text{H}_4\text{SCH}_3$ ,  $\text{Os}_3(\text{CO})_{11}\text{PPh}_2\text{C}_6\text{H}_4\text{SCH}_3$ ,  $\text{Os}_3(\text{CO})_{11}\text{Ph}_2\text{PCH}_2\text{SPh}$ ,  
 dan gugusan dwitertukarganti  $\text{Os}_3(\text{CO})_{10}\text{Ph}_2\text{PCH}_2\text{SPh}$ . Tambahan pula, empat  
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 $\text{Ru}_3(\text{CO})_9(\text{dppm})\text{PPh}_2\text{C}_6\text{H}_4\text{SCH}_3$ ,  $\text{Ru}_3(\text{CO})_9(\text{dpam})\text{PPh}_2\text{C}_6\text{H}_4\text{SCH}_3$  dan  $\text{Ru}_3(\text{CO})_9$   
 $(\text{dotpm})\text{Ph}_2\text{PCH}_2\text{SPh}$  dari reaksi  $\text{Ru}_3(\text{CO})_{10}(\text{LL})$  dengan dua P, S ligan. Ligan  
 monodentat dan ligan bidentat menduduki kedudukan khatulistiwa atas sebab  
 sterik. Ikatan Ru-Ru yang paling panjang adalah *cis* kepada ligan P, S  
 monodentat melainkan bagi gugusan  $\text{Os}_3(\text{CO})_{10}\text{Ph}_2\text{PCH}_2\text{SPh}$  ikatan Ru-Ru yang  
 paling panjang adalah ikatan di antara ligan bidentat P, S. Untuk semua gugusan,  
 ikatan Ru-C pada kedudukan paksi lebih panjang daripada CO pada kedudukan  
 khatulistiwa. Tindak balas  $\text{Ru}_3(\text{CO})_{10}(\text{LL})$ , dengan empat asetilena hujung yang  
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 $(\text{C}_2\text{Si}(\text{CH}_3)_3)]$ ,  $[\text{HRu}_3(\text{CO})_7(\text{dpae})(\text{C}_2\text{Si}(\text{CH}_3)_3)]$ ,  $[\text{HRu}_3(\text{CO})_7(\text{dppm})(\text{C}_2(\text{C}_6\text{H}_4)\text{-4-OCH}_3)]$ ,  
 $[\text{HRu}_3(\text{CO})_7(\text{dppe})(\text{C}_2(\text{C}_6\text{H}_4)\text{-4-OCH}_3)]$ ,  $[\text{HRu}_3(\text{CO})_7(\text{dppf})$   
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 $(\text{dpam})(\text{C}_2\text{C}(\text{CH}_3)_3)]$ ,  $[\text{HRu}_3(\text{CO})_7(\text{dpam})(\text{C}_2(\text{C}_6\text{H}_4)\text{-4-CH}_3)]$ . Suatu struktur yang  
 unik triruthenium terbuka  $[\text{Ru}_3(\text{CO})_9(\text{dpam})(\text{COC}_6\text{H}_5)]$ , adalah  $(\text{COC}_6\text{H}_5)$  asil  
 berhubung kepada Ru1---Ru3. Selain itu, atom arsenik kedua, AS(2) juga  
 berhubung kepada Ru1---Ru3. Tindak balas  $\text{Ru}_3(\text{CO})_{12}$  dengan kedua-dua ligan  
 antimoni;  $\text{Sb}(\text{C}_6\text{H}_4\text{-3-OCH}_3)_3$  dan  $\text{Sb}(\text{C}_{12}\text{H}_9)_3$  menghasilkan dua kelompok  
 triruthenium terbuka  $\text{Ru}_3(\text{CO})_{10}(\text{COC}_6\text{H}_4\text{-3-OCH}_3)\text{Sb}(\text{C}_6\text{H}_4\text{-3-OCH}_3)_2$  dan  
 $[\text{Ru}_3(\text{CO})_{10}(\text{COC}_{12}\text{H}_9)(\text{Sb}(\text{C}_{12}\text{H}_9)_2)]$ .  $(\text{COC}_6\text{H}_4\text{-3-OCH}_3)$  dan  $(\text{CO C}_{12}\text{H}_9)$  asil

berhubung kepada Ru1---Ru3. Tambahan pula, tindak balas  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$ ,  $\text{Ru}_3(\text{CO})_{10}(\text{dpae})$  dengan dua ligan antimoni; menghasilkan tiga kelompok tritertukarganti  $[\text{Ru}_3(\text{CO})_9(\text{dppm})(\text{Sb}(\text{C}_6\text{H}_4\text{-3-OCH}_3)_3)]$ ,  $[\text{Ru}_3(\text{CO})_9(\text{dpae})(\text{Sb}(\text{C}_6\text{H}_4\text{-3-OCH}_3)_3)]$ , dan  $[\text{Ru}_3(\text{CO})_9(\text{dppm})(\text{Sb}(\text{C}_{12}\text{H}_9)_3)]$ . Ikatan Ru-Ru paling panjang adalah *cis* kepada ligan antimoni monodentat. Bagi semua kelompok, ikatan Ru-C lebih panjang pada kedudukan CO paksi daripada CO khatulistiwa.

**SYNTHESIS AND CHARACTERISATION OF NEW Ru<sub>3</sub> AND Os<sub>3</sub>  
CLUSTERS WITH SULPHUR CONTAINING PHOSPHINES, ALKYNE,  
AND ANTIMONY LIGANDS**

**ABSTRACT**

Twenty four new clusters; twenty one new triruthenium carbonyl clusters, three triosmium carbonyl clusters, and four new ligands were successfully synthesised and characterised by elemental analysis and spectroscopic methods, including IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR spectroscopy. Molecular structures of the crystallised products were determined by single crystal X-ray diffraction except for Ru<sub>3</sub>(CO)<sub>10</sub>(dpae). Two isomer ligands of C<sub>19</sub>H<sub>17</sub>PS; namely PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SMe and Ph<sub>2</sub>PCH<sub>2</sub>SPh, two antimony ligands Sb(C<sub>6</sub>H<sub>4</sub>-3-OCH<sub>3</sub>)<sub>3</sub> and Sb(C<sub>12</sub>H<sub>9</sub>)<sub>3</sub> were used to form clusters. One antimony compound [Sb((C<sub>6</sub>H<sub>4</sub>)SCH<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>], was tested for its anticancer potential against several human cancerous cell lines, namely colon (HCT- 116 and HT-29), breast (MCF-7) and Leukemia (K-562) cell lines. Human normal colon cells (CCD-18Co) as control were used as a model cell line for normal cells. The result revealed that the tested compound showed promising antiproliferative effects on all cancer cell lines. The result of cytotoxicity test could be a good lead for drug discovery. The reaction of Ru<sub>3</sub>(CO)<sub>12</sub> and Os<sub>3</sub>(CO)<sub>12</sub> with the sulphur containing phosphines bidentate ligands produced three monosubstituted clusters; [Ru<sub>3</sub>(CO)<sub>11</sub>(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SCH<sub>3</sub>)], [Os<sub>3</sub>(CO)<sub>11</sub>

$(PPh_2C_6H_4SCH_3)]$ ,  $[Os_3(CO)_{11}(Ph_2PCH_2SPh)]$ , and one disubstituted cluster,  $[Os_3(CO)_{10}(Ph_2PCH_2SPh)]$ . Furthermore, four trisubstituted clusters  $[Ru_3(CO)_9(dppe)(PPh_2C_6H_4SCH_3)]$ ,  $[Ru_3(CO)_9(dppm)(PPh_2C_6H_4SCH_3)]$ ,  $[Ru_3(CO)_9(dpam)(PPh_2C_6H_4SCH_3)]$ , and  $[Ru_3(CO)_9(dotpm)(Ph_2PCH_2SPh)]$  were obtained from the reaction of  $[Ru_3(CO)_{10}(LL)]$  with the sulphur containing phosphines bidentate ligands. Monodentate and bidentate ligands occupy the equatorial position for a steric reason. The longest Ru-Ru bond is *cis* to the sulphur containing phosphines ligands. Except for  $[Os_3(CO)_{10}(Ph_2PCH_2SPh)]$ , the longest Ru-Ru bond is the bond between the bidentate sulphur containing phosphines ligands. For all the clusters, the Ru-C bonds are longer for axial CO than equatorial CO. The reaction of  $[Ru_3(CO)_{10}(LL)]$ , with four different terminal acetylenes namely  $HC_2Si(CH_3)_3$ ,  $HC_2(C_6H_4)-4-OCH_3$ ,  $HC_2C(CH_3)_3$ , and  $HC_2(C_6H_4)-4-CH_3$  produced  $[HRu_3(CO)_7(dppe)(C_2Si(CH_3)_3)]$ ,  $[HRu_3(CO)_7(dppf)(C_2Si(CH_3)_3)]$ ,  $[HRu_3(CO)_7(dpae)(C_2Si(CH_3)_3)]$ ,  $[HRu_3(CO)_7(dppm)(C_2(C_6H_4)-4-OCH_3)]$ ,  $[HRu_3(CO)_7(dppe)(C_2(C_6H_4)-4-OCH_3)]$ ,  $[HRu_3(CO)_7(dppf)(C_2(C_6H_4)-4-OCH_3)]$ ,  $[HRu_3(CO)_7(dpae)(C_2(C_6H_4)-4-OCH_3)]$ ,  $[HRu_3(CO)_7(dpam)(C_2C(CH_3)_3)]$ , and  $[HRu_3(CO)_7(dpam)(C_2(C_6H_4)-4-CH_3)]$ . A novel compound of open triruthenium  $[Ru_3(CO)_9(dpam)(COC_6H_5)]$ , the  $(COC_6H_5)$  acyl is bridging Ru(1)---Ru(3) atoms. The second arsenic atom, As(2) is also bridging Ru(1)---Ru(3) atoms. The reaction of  $Ru_3(CO)_{12}$  with the two antimony ligands,  $Sb(C_6H_4-3-OCH_3)_3$  and  $Sb(C_{12}H_9)_3$  produced two open triruthenium clusters  $[Ru_3(CO)_{10}(COC_6H_4-3-OCH_3)(Sb(C_6H_4-3-OCH_3)_2)]$  and  $[Ru_3(CO)_{10}(COC_{12}H_9)(Sb(C_{12}H_9)_2)]$ . The  $(COC_6H_4-3-OCH_3)$  and  $(COC_{12}H_9)$  acyl are bridging

Ru(1)---Ru(3) atoms. Furthermore, the reaction of  $[\text{Ru}_3(\text{CO})_{10}(\text{dppm})]$ ,  $[\text{Ru}_3(\text{CO})_{10}(\text{dpae})]$  with the two antimony ligands; produced three trisubstituted clusters  $[\text{Ru}_3(\text{CO})_9(\text{dppm})(\text{Sb}(\text{C}_6\text{H}_4\text{-3-OCH}_3)_3)]$ ,  $[\text{Ru}_3(\text{CO})_9(\text{dpae})(\text{Sb}(\text{C}_6\text{H}_4\text{-3-OCH}_3)_3)]$ , and  $[\text{Ru}_3(\text{CO})_9(\text{dppm})(\text{Sb}(\text{C}_{12}\text{H}_9)_3)]$ . The longest Ru-Ru bond is *cis* to the monodentate antimony ligand. For all the clusters, the Ru-C bonds are longer for axial CO than equatorial CO.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Metal clusters chemistry

Intensive study of the chemistry of transition metal clusters started in the middle of the last century. Organometallic cluster chemistry lies as a link between pure organic and inorganic chemistry as it involves the influence of inorganic metal ions and organic molecules or organic functional groups. The metal cluster provides a framework in which ligands are capable of coordination with one or more metal centres [1].

Cluster molecules are formed from the coordination of  $\pi$ -acceptor ligands and transition metal atoms, in particular, ligands such as carbon monoxide, cyclopentadienyl, and phosphine. The  $\pi$ -acceptor ligands help to produce the most stable condition for the metal-metal bond formation of the Group 8 elements by inducing the high overlap between the atomic orbitals of the metal. The formation of metal-metal bonds is necessary to construct cluster complexes. The bonding between metal and carbon monoxide, always involves coordination of the carbon atom, through the donation of the 2e on the carbon atom to an empty metal d orbital of  $\sigma$  symmetry, and a back donation from filled metal d orbitals to the empty  $\pi^*$  C-O antibonding orbital.



A cluster defined as a molecule containing three or more metal atoms connected by direct metal-metal bonds. Triruthenium dodecacarbonyl  $\text{Ru}_3(\text{CO})_{12}$  and triosmium dodecacarbonyl  $\text{Os}_3(\text{CO})_{12}$ , have three metal atoms linked by the metal - metal bond. Each Ru and Os atom carries four terminal carbonyl ligands. Two carbonyl ligands are equatorial because parallel to the plane of the  $\text{Ru}_3$  and  $\text{Os}_3$  triangle, the other two are axial because they are vertical to the  $\text{Ru}_3$  and  $\text{Os}_3$  triangle [2].

The type of ligands can also affect the nuclearity and geometry of the cluster by extending its steric effect. For example, as the ligand size increases, the rates of reactions leading to metal-metal bond formation are reduced and for a given ligand: metal ratio, the higher-nuclearity clusters are destabilised by ligand-ligand repulsion effects [3].

The properties of the metal cluster that are built from three or more metal centre help to facilitate activation and transformation of the substrates and high mobility of the ligands could promote reactions between several molecules bonded to the cluster framework [2]. The study of the metal clusters is interesting mostly because metal clusters can act as homogeneous catalysts [4,5]. The metal cluster has played a significant role in many chemical reactions, for example, they act as catalysts for carbonylation of alcohols [6,7], hydrogenation, isomerization of olefins [6–10], and water gas shift reaction and hydroformylation of alkenes [11].

These clusters of triruthenium and triosmium are of concern in the oil industry, especially those containing large amounts of sulphur compounds that require

hydrodesulphurisation (HDS) and hence are of interest environmentally and industrially [12–15]. Ruthenium compounds show anticancer activities and reduce the potential for tumour resistance and can be a significant chemotherapy for cancer cells [16–20].

### **1.1.1 Triiron Dodecacarbonyl**

Triiron dodecacarbonyl was first synthesised in 1906 by the thermal decomposition of  $\text{Fe}_2(\text{CO})_9$ . In 1930 Hieber and Becker synthesised  $\text{Fe}_3(\text{CO})_{12}$  from freezing point depression studies in iron pentacarbonyl solvent. In 1951 it was characterised as  $\text{Fe}_3(\text{CO})_{12}$  by Sheline. In 1968, Wei and Dahl characterised and formulated  $\text{Fe}_3(\text{CO})_{12}$  consisting of three identical  $\text{Fe}(\text{CO})_3$  and linked in pairs to one another by a bridging carbonyl group and an iron-iron bond [21].

### **1.1.2 Triruthenium dodecacarbonyl**

Triruthenium dodecacarbonyl was synthesised in 1910 by Mond and co-workers, from the reaction of ruthenium metal with carbon monoxide at 300 °C and 400 atmosphere pressure. The product obtained was a triruthenium carbonyl, but it was not correctly characterised [22]. Then, Corey and Dahl in 1961 characterised and formulated it as  $\text{Ru}_3(\text{CO})_{12}$  by X-ray crystallography [23]. In 1966, Bruce and Stone published an improved synthesis of  $\text{Ru}_3(\text{CO})_{12}$  by carbonylation of ruthenium trichloride in methanol at 65°C and less than 10 atmosphere pressure in the presence of halogen acceptors [24]. Later in 1983, Bruce and co-workers reported a new

preparation of  $\text{Ru}_3(\text{CO})_{12}$  by the carbonylation of a 1% methanol solution of hydrated ruthenium trichloride at 50-60 atmosphere pressure and 125 °C for 16–18 h [25].

### 1.1.3 Triosmium dodecacarbonyl

Triosmium dodecacarbonyl was synthesised in 1943 by Hieber, as  $\text{Os}_2(\text{CO})_9$ . The reaction of  $\text{OsO}_4$  with HI gave an oxy iodide, which was treated with Ag powder in benzene with carbon monoxide at 150 °C and (200 atm) to give  $\text{Os}_3(\text{CO})_{12}$  in poor yield. Corey and Dahl in 1961 characterised and formulated it as  $\text{Os}_3(\text{CO})_{12}$  by X-ray crystal structure [23]. Triosmium dodecacarbonyl has been one of the opener compounds in the evolution of transition-metal clusters, because it can produce a lot of new clusters, often without any change of nuclearity. Triosmium dodecacarbonyl reactive derivatives;  $\text{Os}_3\text{H}_2(\text{CO})_{10}$  [10],  $\text{Os}_3(\text{CO})_{11}\text{L}$ , and  $\text{Os}_3(\text{CO})_{10}\text{LL}$  are useful starting material for triosmium Clusters, and hundreds of compounds had been produced, where L and LL are labile ligands [26].

Many types of ligands have the potential to substitute with these transition metal carbonyl clusters, depending on the coordination reactivity of these ligands [2]. This contribute to an idea of substituting different ligands with a variety of chemical and physical properties to transition metal carbonyl clusters.

## 1.2 Ligands

Ligands are neutral molecules or ions that bond to a central metal atom or ion to form a complex. Ligands donate a pair of electrons or more (Lewis bases), and the central atom receives the pair of electrons or more (Lewis acid). Ligands are classified due to the number of donor atoms as monodentate, bidentate, and polydentate. They are also classified as cations, anions, or neutral molecules [27].

### 1.2.1 Bidentate ligands (L-L) Types (P- P) and (As-As)

Bidentate ligands are defined as ligands that can form two bonds with metals. An important Group 15 ligand is bidentate phosphine and arsine that contains a carbon backbone linking the Group 15 element. For example, the most common bidentate phosphine ligands are of the type  $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$ , where  $n = 1-6$  which have been widely used in organometallic reactions over the years [28–33]. Also, bidentate ligands can possess two different Group 15 donor atoms known as a mixed bidentate ligand. For example, the arphos ligand with chemical formula,  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$ , is a mixed bidentate ligand with As and P atoms linked by two methylene carbon backbone [31].

Bidentate ligands can play a role in stabilising metal cluster by coordinating in different modes. The bidentate ligand has been found to arrange a variety of bonding modes on the cluster, including monodentate, chelating a single metal atom in the cluster, bridging across a metal-metal bond, and forming an intermolecular link

across two triangle clusters. Reactions conducted by Bruce and co-workers in 1982 which deal with  $\text{Ru}_3(\text{CO})_{12}$  and bis(diphenyl phosphino)ethane (dppe) were reported to function as a monodentate, bidentate and chelating ligand. Moreover, they served as a bridging ligand across a metal-metal bond, connecting a ligand in the cluster.  $[\text{Ru}_3(\text{CO})_{11}]_2\text{dppe}$ ,  $[\text{Ru}_3(\text{CO})_{11}]_2\text{dppb}$ , and  $[\text{Ru}_3(\text{CO})_{11}]_2\text{dppf}$ , whereby two metal cluster units bonded through di-tertiary phosphine ligands [28,34,35]. Particularly, diphosphines such as dppm, dppe, dppf, dcpm, and dpam are in widespread use in homogeneous catalysis [31,36].

The design, synthesis, and characterization of metal cluster complexes are essential in providing a suitable array of the cluster that contains the necessary stoichiometry and binding required for understanding the electronic influence as well as the effect of the different ligands on the chemical behaviour of their cluster complexes. Nevertheless, metal clusters showed a significant role in the industry as homogeneous catalysts [5,37]. Moreover, as precursors to bi- and trimetallic nanoparticle catalysts in heterogeneous catalysis[38], detailed knowledge of the bonding and geometry structure of these clusters are needed in providing a route from fundamental to applied science in this area of study. Research about the synthesis, characterization and molecular structure which are resulted from the substitution of CO with diphosphine and diarsine ligands are necessary to understand the electronic and steric effects of the new cluster.

### 1.2.2 Sulphur containing phosphines ligands

In fact, a ligand containing one strongly binding donor atom and one weakly binding donor atom are used to maintain an active site at a metal centre until it is required to effect a transformation of a substrate. Ligands containing phosphorus centres and sulphur centres are significant. Both phosphorus and sulphur are common ligand donor atoms for a broad range of metals while the existence of several lone pairs of electrons and the low ionisation energy of sulphur offers the possibility of a rich sulfur-based chemistry of the complexes [37].

The (P, S) ligands with  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$  react as monodentate, through phosphorus [13,15,39,40], and as bidentate ligands bridging or chelating through phosphorus and sulphur [12–14,41–43]. Phosphorus atom in (P, S) ligands donates 2 electrons when bonded to one metal atom, 3 electrons when bridging two metal atoms, and has the priority to connect with triruthenium and triosmium. Phosphorus ligands are strong  $\sigma$ -donors and poor  $\pi$ -acceptors [2]. Sulfur in (P, S) ligands can donate; 2 electrons, when bonded to one metal atom [42,43], 3 electrons ( $\mu_2$ ) when bridging two metal atoms [12,14,41], 4 electrons ( $\mu_3$ ) [41] and 5 electrons ( $\mu_3$ ) when capping three metal atoms [44].

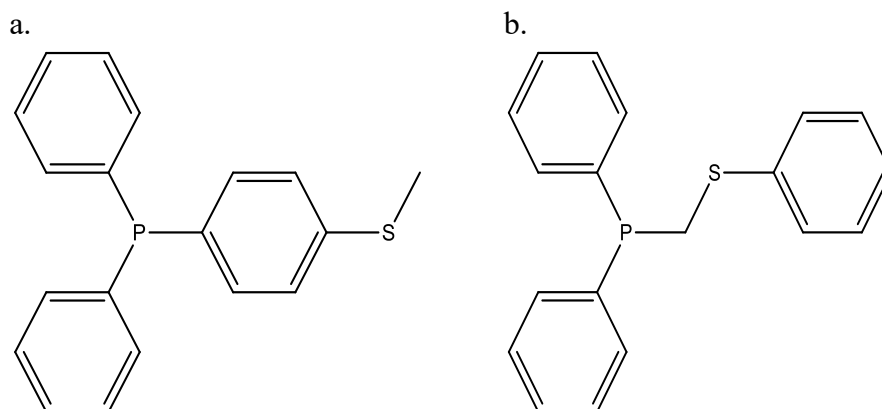


Figure 1.1 a)  $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{SCH}_3$  and b)  $\text{Ph}_2\text{PCH}_2\text{SPh}$ .

### 1.2.3 Alkyne ligands

The reactions of terminal alkynes with trinuclear ruthenium clusters lead to hydrogen transfer to the metals centre [45]. The alkyne ligands react with triruthenium dodecacarbonyl to give clusters containing  $\mu\text{-H}$  and  $\mu\text{-alkynyl}$  group. Alkynyl group donate 5 electrons through two types of bonds,  $\text{Ru-C}$   $\sigma$ -bond, donate 1 electron and the  $\text{C}\equiv\text{C}$  bond bridging the other two Ru atoms by  $\pi$  bonds, donate 4 electrons. The  $\mu\text{-H}$  located between the same two Ru atoms which are connected to  $\text{C}\equiv\text{C}$  bond by  $\pi$  bonds. The  $\text{HC}\equiv\text{CR}$  is then considered as a 6 electrons donor ligand [46]. The triruthenium alkynes clusters are interesting because they acted as catalysts or catalyst precursors in hydrogenation [47], their theoretical studies[45], their biological activities as an anticancer drug[48], and they have redox centres, such as the ferrocenyl group[49].

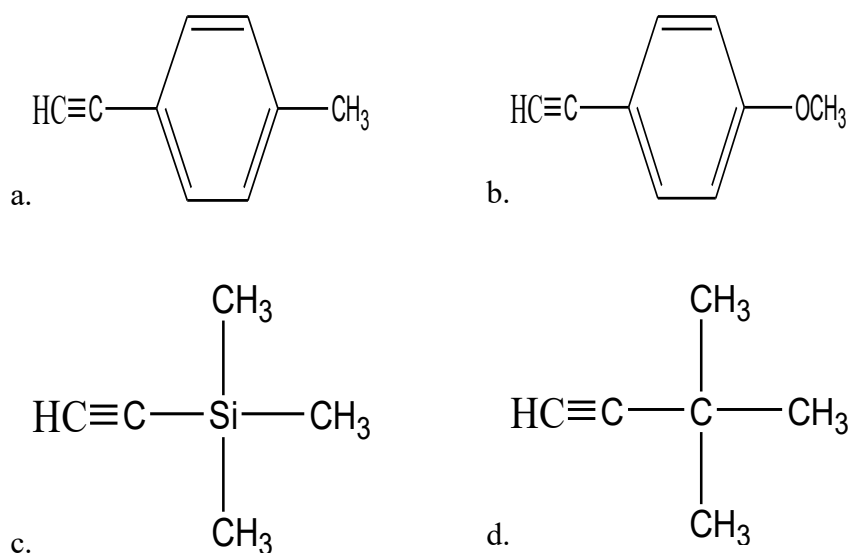


Figure 1.2 a)  $\text{CH}_3-4-\text{C}_6\text{H}_5\text{C}_2\text{H}$ , b)  $\text{CH}_3\text{O}-4-\text{C}_6\text{H}_5\text{C}_2\text{H}$ , c)  $(\text{CH}_3)_3\text{SiC}_2\text{H}$ , and d)  $\text{HC}_2\text{C}(\text{CH}_3)_3$

#### 1.2.4 Antimony ligands

Antimony was found as antimony trisulphide in nature. The antimony compounds is used for cosmetics. The main application for antimony metal is to be involved in some alloys; it is alloyed with lead or other metals to improve strength and hardness. Lead antimony alloy is also used for lead acid batteries plates and solder alloy. Antimony in the electronics industry is used to produce some semiconductor devices, such as diodes and infrared detectors. Antimony compounds are used to produce flame-retardant materials such as paints and glass [50]. Organometallic chemistry clusters containing transition metals and main group atoms are interesting, because they have the function of different properties of transition metals, and the main group atoms and may give rise to some unique chemistry [1]. Structural reports on carbonyl clusters containing ruthenium and antimony show a few structures in the



Cambridge Crystallographic Database [51–54]. Triruthenium carbonyl and their substituted compounds are of interest due to their catalytic and biological activities [54].

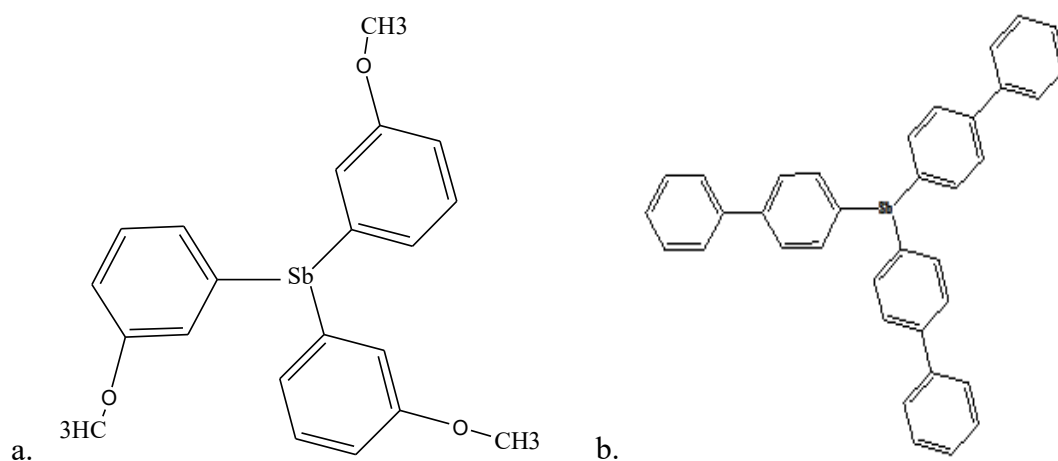


Figure 1.3 a)  $\text{Sb}(\text{C}_6\text{H}_4\text{-3-OCH}_3)_3$  and b)  $\text{Sb}(\text{C}_{12}\text{H}_9)_3$

### 1.2.5 Objectives

1. To synthesise new (P, S) and antimony ligands and study the ligands' ability to act as bidentate and reactivity towards  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Os}_3(\text{CO})_{12}$ , and  $\text{Ru}_3(\text{CO})_{10}(\text{LL})$ .
2. To synthesise new complexes of triruthenium and triosmium clusters containing alkyne, phosphorus and sulphur containing, and antimony ligands
3. To characterise all new compounds through various analytical methods including infrared spectroscopy (IR), nuclear magnetic resonance (NMR), CHN analysis, X-ray diffraction (XRD) and determine the molecular structures of new metal cluster

complexes. In addition, a study reactivity or biological activities of these compounds will be performed.

### 1.2.6 Scope of the present investigation

This study is on the synthesis of new compounds by substituting carbonyl ligand in  $\text{Ru}_3(\text{CO})_{12}$  with (P, S), alkyne, and antimony ligands and  $\text{Os}_3(\text{CO})_{12}$  with (P, S) ligands. Also, compounds of the type  $\text{Ru}_3(\text{CO})_{10}(\text{LL})$  [where LL= (dppm), (dpam), (dppe), (dppf), (dotpm), and (dpae) were synthesized.

Two sulphur containing phosphines ligands were chosen; (4-(methylthio) phenyl)diphenyl phosphino,  $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4) \text{SCH}_3$  and diphenyl (phenylthiomethyl) phosphine,  $\text{Ph}_2\text{PCH}_2\text{SPh}$  to study the ligands' ability to act as bidentate and their reactivities towards  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$ .

Four alkyne ligands were used; (trimethylsilyl)acetylene,  $(\text{CH}_3)_3\text{SiC}_2\text{H}$ , tertbutylacetylene,  $\text{HC}_2\text{C}(\text{CH}_3)_3$ , *paratolyl*acetylene,  $\text{CH}_3\text{-4-C}_6\text{H}_5\text{C}_2\text{H}$ , and *paramethoxy phenyl*acetylene,  $\text{CH}_3\text{O-4-C}_6\text{H}_5\text{C}_2\text{H}$  to study the reactivities of these ligands towards  $\text{Ru}_3(\text{CO})_{10}(\text{LL})$  compounds and synthesize actylene clusters of type  $\text{HRu}_3(\text{CO})_7(\text{LL})(\text{C}_2\text{R})$ .

Two new and novel antimony ligands were synthesised, namely, tris *meta* methoxyphenylantimony,  $\text{Sb}(\text{C}_6\text{H}_4\text{-3-OCH}_3)_3$  and tris biphenylantimony,  $\text{Sb}(\text{C}_{12}\text{H}_9)_3$ .

A study of their reactivities towards  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$ , and  $\text{Ru}_3(\text{CO})_{10}(\text{dppe})$  compounds.

All the new synthesised cluster complexes were characterised using infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), CHN analysis and single crystal X-ray diffraction (XRD). IR is one of the first spectroscopic techniques applied to the study of carbonyl clusters with its capability in identifying carbonyl stretching and other functional groups. CHN analysis is used to determine the exact composition of carbon, hydrogen, and nitrogen elements within the compound. NMR is spectroscopic technique determining the chemical shift of  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  nuclei in the cluster complexes. A single crystal X-ray diffraction (XRD) study is required to obtain more detailed and accurate information about the atomic molecular and geometric parameters. It is clear that these studies enabled us to make a detailed comparison of the molecular geometries which resulted from the substitution of CO by (P, S), acetylene, and antimony ligands. Furthermore, they allow the exploration of the chemical properties of the novel clusters. Moreover, the establishment of such novel clusters presents new opportunities in both fundamental science and its application.

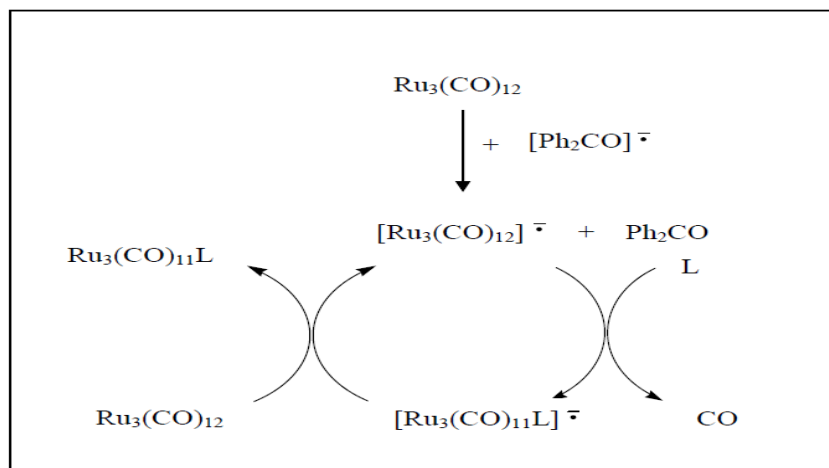
## CHAPTER 2

### LITERATURE REVIEW

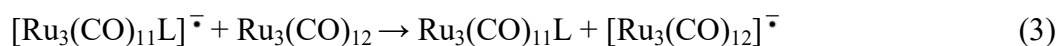
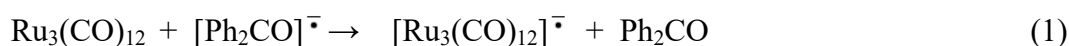
#### 2.1 Carbonyl substitution

Triruthenium dodecacarbonyl reacts with phosphorus, arsenic, and antimony ligands through various methods of substitution reactions. The initial studies on  $\text{Ru}_3(\text{CO})_{12}$  substituted by  $\text{PPh}_3$  afforded  $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$  using the thermal method [55]. Candlin and Shortland studied the thermal substitution of CO by  $\text{PPh}_3$ ,  $\text{PPh}_2(\text{C}_2\text{H}_5)$ ,  $\text{PPh}(\text{C}_2\text{H}_5)_2$ ,  $\text{P}(\text{C}_4\text{H}_9)_3$ , and  $\text{P}(\text{OPh})_3$  in  $\text{Ru}_3(\text{CO})_{12}$ . These reactions were reported to give only the tris-substituted complexes with no proof of the mono- or bis-substituted species [29,56].

Study on reactions of  $\text{Pt}(\text{PPh}_3)_4$ , or  $\text{Pt}(\text{PPh}_3)_2(\text{olefin})$  with  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$  where different types of expected products were reported [57]. These reactions are also excellent sources of the clusters type  $\text{Ru}_3(\text{CO})_{12-n} \text{L}_n$  ( $n = 1, 2$ , or  $3$ ) [57]. Bruce et al. and Rieger et al. reported that CO substitution can be catalysed by Na/benzophenone radical anion [55,58,59]. Bruce and co-workers had introduced new methods to activate  $\text{Ru}_3(\text{CO})_{12}$  using sodium benzophenone ketyl radical anion to encourage specific carbonyl substitution of the metal clusters. This substitution involves an electron transfer catalysed (ETC) process. The proposed mechanism of the electron transfer process with  $\text{Ru}_3(\text{CO})_{12}$  is shown in following Scheme [28,29,55,60].



Scheme 2.1 catalytic cycle of benzophenone ketyl anion reaction mechanism [60].



The radical anion  $[\text{Ru}_3(\text{CO})_{12}]^{\bullet -}$ , becomes a reactive species, where the extra electron is in antibonding orbital, leading to a weakened Ru-Ru metal bond. This bond is cleaved, leaving a 17 electron centre, which will be attacked by the ligand resulting in the elimination of CO. The reformation of the metal-metal bond yields a substituted radical anion  $[\text{Ru}_3(\text{CO})_{11}\text{L}]^{\bullet -}$ , which transfers an electron to an unsubstituted ruthenium cluster to continue the catalytic cycle. The requirements for this reaction to occur are that the cluster carbonyl needs to reduce without fragmentation, and the resulting radical has to have a long enough lifetime to allow for substitution. The substituting ligand must be a higher Lewis

base than the carbonyl ligand. Secondly, the ligand must not be reduced by the diphenylketyl radical anion. When these conditions are met, this method allows for short reaction times, mild conditions, high product yields and also leads to the isolation of many complexes that were previously difficult to obtain. These techniques provide a convenient platform for preparation of a variety of substitution products. For example, the utility of this technique was shown in synthesising some mono, di- and tri-substituted cluster complexes of  $\text{Ru}_3(\text{CO})_{12}$  [29].

Bis(triphenylphosphine)iminium (acetate/cyanide)  $[\text{PPN}][\text{OAc}]$  or  $[\text{PPN}][\text{CN}]$  activate  $\text{Ru}_3(\text{CO})_{12}$  towards specific CO substitution. Lavinge and Kaesz discovered that the catalytic amount of  $[\text{PPN}][\text{OAc}]$  in the reaction would support substitution by tertiary phosphine such as  $\text{PPh}_3$ , dppm, and dppe [61]. Cullen et al. also, studied the catalytic reaction for dppf using  $[\text{PPN}][\text{OAc}]$  [62]. Therefore, other  $[\text{PPN}]^+$  salts show varying degrees of activities, and rates of ligand substitution in  $\text{Ru}_3(\text{CO})_{12}$  enhanced by the addition of methoxide ion, which formed the labile methoxycarbonyl complex  $[\text{Ru}_3(\text{CO}_2\text{Me})(\text{CO})_{11}]$  [63]. These methods reveal that such complexes have a higher reactivity towards nucleophilic reagents, undergoing carbonyl substitution reactions and nucleophilic additions to coordinated CO ligands under very mild conditions [64].

Trimethylamine N-oxide,  $\text{Me}_3\text{NO}$  activates the replacement of carbonyl in  $\text{Ru}_3(\text{CO})_{12}$  in the presence of a labile ligand such as acetonitrile  $\text{MeCN}$ , which is

replaced very fast. These complexes  $[\text{Ru}_3(\text{CO})_{11}(\text{MeCN})]$  and  $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$  were prepared at low temperature [65]. The use of  $\text{Me}_3\text{NO}$  to remove co-ordinated carbon monoxide was first reported by Shvo and Hazum [66].

The photochemical initiator is the most interesting applications of these photogenerated reducing agents. The electron transfer (ETC) catalysed carbonyl substitution of  $\text{Ru}_3(\text{CO})_{12}$  produces  $[\text{Ru}_3(\text{CO})_{11}(\text{PMe}_2\text{Ph})] + \text{CO}$  [67]. In 1986 a comprehensive investigation of the medium, ligand, and wavelength effects on the quantum yields and flash photolysis kinetics for the photo-fragmentation and photosubstitution reactions of the  $\text{Ru}_3(\text{CO})_{12}$  was reported [68]. For example studied of the substituted clusters of type  $\text{Ru}_3(\text{CO})_{12-n} \text{L}_n$ , ( $\text{L} = \text{P}(\text{OCH}_3)_3$ ,  $\text{PPh}_3$ ,  $\text{P}(\text{p-tolyl})_3$ , or  $\text{P}(\text{O(o-tolyl)})_3$ ). These results were interpreted regarding the following model for  $\text{Ru}_3(\text{CO})_{12}$  photochemistry. Photo-fragmentation (e.g.,  $\text{Ru}_3(\text{CO})_{12} + 3\text{L} \rightarrow 3\text{Ru}(\text{CO})_4\text{L}$ ) occurs mainly from the lowest energy excited state and proceeds via an intermediate isomeric to  $\text{Ru}_3(\text{CO})_{12}$  but not a diradical. It was proposed to have one coordinatively unsaturated ruthenium centre trappable by a two-electron donor, i.e.,  $\text{L}$ , to produce a second intermediate  $\text{Ru}_3(\text{CO})_{12}\text{L}$  which is the precursor to the photo-fragmentation products. This reaction (e.g.  $\text{Ru}_3(\text{CO})_{12} + \text{L} \rightarrow [\text{Ru}_3(\text{CO})_{11}\text{L}] + \text{CO}$ ) was proposed to occur largely from higher energy states through CO dissociation to produce the unsaturated intermediate  $\text{Ru}_3(\text{CO})_{11}$ . Moreover, the photolysis was dependent on

the nature of L, and photolysis studies established the reactivity of this species with different L to follow the order  $\text{CO} > \text{P}(\text{OCH}_3)_3 > \text{PPh}_3$  [68].

$\text{Os}_3(\text{CO})_{12}$  is more stable than  $\text{Ru}_3(\text{CO})_{12}$  and many reactions can be carried out without any change of nuclearity.  $\text{Os}_3$  systems are often quite stable to air and heat and easily crystallised [26]. Thermal reactions involving  $\text{Os}_3(\text{CO})_{12}$  and phosphines or arsines ligands produced a mixture of mono-, di-, and tri-substituted of triosmium clusters, by controlling the stoichiometry, a good yield of the product can be obtained in using chromatography separation. Chemical activation of  $\text{Os}_3(\text{CO})_{12}$  can be carried out with Na/benzophenone radical anion [60]. Also, chemical activation of  $\text{Os}_3(\text{CO})_{12}$  with  $\text{Me}_3\text{NO}$ , which was first introduced by Shvo and Hazum removing CO groups through the formation of  $\text{CO}_2$  [66]. Since phosphine and arsine are also susceptible to oxidation by  $\text{Me}_3\text{NO}$ , the direct reaction of  $\text{Os}_3(\text{CO})_{12}$  with phosphine/arsine in the presence of  $\text{Me}_3\text{NO}$  was reported. Substitution of  $\text{Os}_3(\text{CO})_{12}$  derivatives containing labile ligands is the most useful method for preparing mono- and di-substituted phosphines derivatives. Activation of  $\text{Os}_3(\text{CO})_{12}$  by  $\text{Me}_3\text{NO}$  in the presence of a labile ligand such as MeCN, has been used to prepare  $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$  and  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  [42]. Other chemical activations include the use of  $\text{Pt}(\text{PPh}_3)_4$  and the complexes  $[\text{Os}_3(\text{CO})_{12-n}\text{L}_n]$ , produced from reactions with  $\text{Os}_3(\text{CO})_{12}$  [57,60]. Na/benzophenone radical anion was found to catalyse the substitution of phosphine or arsine on  $\text{Os}_3(\text{CO})_{12}$ . Substitution of  $\text{Os}_3(\text{CO})_{12}$  derivatives containing labile ligands is a useful method for preparing mono- and di-



substituted derivatives. Arsines and phosphines react with these derivatives with great specificity [60].

## 2.2 Bidentate ligands with $\text{Ru}_3(\text{CO})_{12}$

The chemical reactions of diphosphine and diarsine bidentate ligands with  $\text{Ru}_3(\text{CO})_{12}$  started in 1970 and were studied by Cullen and Harbourn. They reported the reactions between  $\text{Ru}_3(\text{CO})_{12}$  with the fluorocarbon-bridged ligands, ffars, ffos, and f<sub>6</sub>fos respectively [69]. Since the initial studies, the substitution chemistry and subsequent reactivities and reaction mechanisms of the type  $[\text{Ru}_3(\text{LL})(\text{CO})_{10}]$  and  $[\text{Ru}_3(\text{LL})_2(\text{CO})_8]$  have been studied extensively.

The bidentate ligands have the potential to bind to a metal centre by chelating a single ruthenium atom within the cluster, by bridging a cluster edge and binding two ruthenium atoms, or by acting as a monodentate ligand with one free atom. In 1977, Cotton and Hanson first reported the synthesis of  $[\text{Ru}_3(\text{CO})_{10}(\text{dppm})]$  from the reaction between  $\text{Ru}_3(\text{CO})_{12}$  and dppm refluxed at 50°C for 36 hours [70].  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$  complex was confirmed by the characteristic pattern of the carbonyl stretching frequencies for disubstituted complexes. Later, Bruce and co-workers reported the synthesis of  $[\text{Ru}_3(\text{CO})_{10}(\text{dppm})]$  at 91% yield using sodium benzophenone ketyl radical [55].

The X-ray structure afforded for  $[\text{Ru}_3(\text{CO})_{10}(\text{dppm})]$  reported by Coleman and co-workers in 15% yield [71]. The interesting abnormality found in this structure was